

AD-A184 318

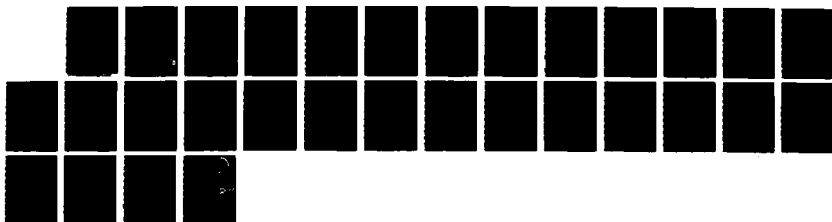
DYNAMICS OF ATOMS IN LOW-SYMMETRY SYSTEMS(U) CORNELL
UNIV ITHACA NY LAB OF ATOMIC AND SOLID STATE PHYSICS
R M NIEMINEN JUL 87 TR-33 N00014-82-K-0576

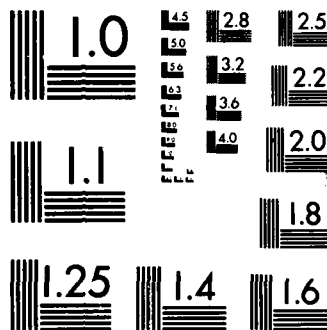
1/1

UNCLASSIFIED

F/G 20/12

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A184 318

DTIC FILE COPY

①

OFFICE OF NAVAL RESEARCH

Contract N00014-82-K-0576

TECHNICAL REPORT NO. 33

DYNAMICS OF ATOMS IN LOW-SYMMETRY SYSTEMS

by

R. M. Nieminen

Laboratory of Atomic and Solid State Physics

Cornell University

Ithaca, New York 14853-2501

July, 1987

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release
and sale; its distribution is unlimited

DTIC
ELECTE
AUG 24 1987
S E D

87

7 21 140

REPORT DOCUMENT

READ INSTRUCTIONS
BEFORE COMPLETING FORM
REPORT'S CATALOG NUMBER

AD-A184 318

1. REPORT NUMBER

33

2. TITLE (and Subtitle)

Dynamics of Atoms in Low-Symmetry Systems

3. TYPE OF REPORT & PERIOD COVERED

Technical

4. PERFORMING ORG. REPORT NUMBER

5. AUTHOR(s)

R. M. Nieminen

6. CONTRACT OR GRANT NUMBER(s)

N00014-82-K-0576

7. PERFORMING ORGANIZATION NAME AND ADDRESS

Laboratory of Atomic and Solid State Physics
Cornell University
Ithaca, NY 148508. PROGRAM ELEMENT, PROJECT, TASK
AREA & WORK UNIT NUMBERS

9. CONTROLLING OFFICE NAME AND ADDRESS

Office of Naval Research
800 Quincy St.
Arlington, VA

10. REPORT DATE

July 1987

11. NUMBER OF PAGES

26

12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

13. SECURITY CLASS. (of this report)

unclassified

14. DECLASSIFICATION/DOWNGRADING
SCHEDULE

15. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale;
its distribution is unlimited.

16. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

17. SUPPLEMENTARY NOTES

18. KEY WORDS (Continue on reverse side if necessary and identify by block number)

19. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Recent ideas to extend the scope and applicability of large-scale computer simulation of condensed phases are discussed. These include (i) the use of simulated annealing and related methods in first-principles calculations and (ii) the development "effective-medium" and similar approximate approaches to interatomic interactions in low-symmetry situations. Examples of applications to molecular dynamics simulations are presented.

Dynamics of Atoms in Low-Symmetry Systems

R. M. Nieminen*

Laboratory of Atomic and Solid State Physics

Cornell University, Clark Hall

Ithaca, N.Y. 14853, USA

Abstract

Recent ideas to extend the scope and applicability of large-scale computer simulation of condensed phases are discussed. These include (i) the use of simulated annealing and related methods in first-principles calculations and (ii) the development "effective-medium" and similar approximate approaches to interatomic interactions in low-symmetry situations. Examples of applications to molecular dynamics simulations are presented.



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

*Permanent address: Laboratory of Physics, Helsinki University of Technology, 02150 Espoo, Finland

1. Introduction

Computer simulation of condensed phases and complex phenomena adds a new important dimension to physics research. In particular, it has proven invaluable in bridging the gap between experiment and theory in those cases where either (or both) of the two is (are) inaccurate, insufficient or fundamentally limited. Moreover, computer simulation vastly extends the scope of model building and testing from the traditional domain of linear equations and analysis to that of nonlinearity, which is more a rule than an exception in nature.

There are actually a multitude of numerical techniques often vaguely referred to as computer simulation or computer experiments. They range from numerical solutions of partial differential equations to Monte Carlo, Langevin and molecular dynamics simulations to path integral evaluations. Likewise, the physical applications include such diverse systems as turbulence and hydrodynamics, lattice gauge theories of quantum chromodynamics, phase transitions and critical phenomena, stochastic dynamics of growth and pattern formation, and electronic, structural and thermodynamic properties of materials. This talk will concentrate on the last one. There has been impressive progress¹ in that area during the last few years, both in the development of algorithms and computer codes and their implementation to large-scale computing, as well as in the development and refinement of useful physical and mathematical concepts and devices. In particular, molecular dynamics simulation² combined with a

proper description of electron-mediated forces, provides a powerful technique for a computer-based microscopic description of interesting and important material properties. I shall discuss (i) the recent ideas on how to systematically go beyond the rigid (pair) potential description of interatomic interactions and make contact with electronic structure calculations for low-symmetry systems and (ii) present selected applications of molecular dynamics simulations to physical problems of current interest.

2. Beyond classical potentials

Molecular dynamics simulations are conceptually simple yet increasingly useful in elucidating the properties of matter in the microscopic to mesoscopic scale. The usefulness and quantitative reliability, however, often hinges on to what extent the force laws between interacting atoms and molecules can be specified. While relatively simple force laws are feasible for such systems as rare gases and polar molecules, descriptions based on few-body forces are not universally applicable in metallic and covalently bonded matter. (Such descriptions may, however, be useful in limited applications as evidenced by the vast body of work on pair potential simulations for metals³ and the recent efforts⁴ in modelling Si and Ge by two-body and three-body forces)

Here I discuss two recent approaches to interatomic interactions. The first is a scheme to perform first-principles electronic structure calculations in parallel

to the atomic dynamics, while the second entails a class of more approximate but computationally fast methods of obtaining the force laws.

2.1. Simulated annealing and related methods

A few years ago algorithms based on thermodynamic concepts were introduced to solve large-dimensional, nonlinear optimisation problems. In a short period of time these techniques, the most famous among which is the simulated annealing⁵ method, have attracted a good deal of attention. Optimisation problems involve a "cost function", which has to be minimized with respect to the relevant parameters (degrees of freedom). Simulated annealing is based on the analogy between minimizing the cost function in an optimisation problem and the physical problem of obtaining a ground state, e.g. the process of growing a good crystal by slow cooling from its melt. In order to avoid defects or glassy areas in the crystal, slow annealing is necessary. This prohibits the system from getting stuck into a local free energy minimum. In the general optimisation problem, this may be accomplished by using e.g. the Metropolis Monte Carlo algorithm to accept random displacements in the parameter space. The temperature enters as a control parameter in the Boltzmann factor, which is adjusted to ensure the passage to the global minimum. As a last step, a steepest-descent quench can be used to lock into the global minimum.

A very important contribution to the simulated annealing ideas for electronic and structural properties is due to Car and Parrinello⁶. They combined

the electronic density-functional Hamiltonian with the ionic kinetic energy into a cost function to be globally minimized. Traditionally, in electronic structure calculations one first minimizes the electronic energy for fixed ionic positions. According to the Born-Oppenheimer principle, the (Hellmann-Feynman) forces on ions can then be evaluated and the system is allowed to relax. This leads to a series of elaborate self-consistent calculations with the necessary matrix diagonalizations. Even with the biggest available computers, such a procedure becomes prohibitively expensive for systems containing more than a dozen or so atoms, as the number of degrees of freedom to be optimised increases. This is so despite the great simplifications provided by *ab initio* pseudopotential theory and local-density approximations for exchange and correlations. Another bottleneck in these calculations is the cost of large matrix diagonalisations, which scale as proportional to M^3 , where M is the total number of basis functions needed to represent the electronic states and charge densities.

Car and Parrinello suggested that the combined cost function of electrons and ions be minimized by using simulated annealing in the phase space of nuclear coordinates and density-functional single-particle electronic wavefunctions. Rather than doing a Monte Carlo-type search, they add a fictitious classical kinetic energy (with an arbitrary mass) to the electronic fields, and derive the Lagrangian equations of motion for both electronic and ionic degrees of freedom. Additional dynamics can be assigned to e.g. the volume and shape of the system. Orthonormality of the electron states is imposed by the technique of Lagrange multipliers. The result is a set of coupled equations of motion, which

can be simultaneously solved for the ion coordinates and the electron fields using standard discrete time-step methods of classical molecular dynamics. Starting from a suitable set of initial conditions, the "temperature" associated with the fictitious classical dynamics of electrons can be gradually lowered so that the system can relax to its global ground state. By adjusting the electron classical "mass" one can (and should) stay in the vicinity of the Born-Oppenheimer surface.

This technique has two important merits. Firstly, it provides a systematic and practical way of combining real molecular dynamics of the ions with interactions truly derived from electronic structure, i.e. no assumptions of the force laws are required. This is very important for looking at such delicate things as structural phase transitions, grain boundary structures⁷, finite temperature structures of clusters⁸ etc. Secondly, as the simulated annealing technique explicitly avoids direct matrix diagonalisation steps, its computational cost for the electronic part of the problem increase only proportionally to MN (N is the number of electrons) as far as the "iterative diagonalisation" is concerned. There are other parts of the calculation such as the orthonormalisation of the occupied states (MN^2), the generation of the charge densities (MN), and the solution of the Poisson equation, which scales as $M \ln M$ (using fast Fourier transforms). However, it is obvious that the Car-Parrinello technique will be the one of choice for very large electronic structure calculations.

in fact, if one freezes the nuclear positions and only looks at the

electronic minimization problem, there probably are even more efficient dynamic method for the purpose of iterative diagonalisation. The cost function is in this case convex (at least for nonmagnetic systems; magnetic ones can exhibit bistability) and steepest-descent techniques⁹ are feasible. Another recent suggestion¹⁰ deals with speeding up the orthonormalisation step. By using Schrödinger dynamics and a Fourier bandpass filter one can quickly sieve out the eigenfrequencies and associated eigenfunctions. For evaluating the total electron density, which usually is the quantity of interest in self-consistent calculations, one can show that the procedure can be optimised to scale as $MN^{3/2}$.

Another aspect of the computational cost of large-scale electronic structure calculations concerns the basis sets used to represent the wavefunctions and densities. Two commonly used basis sets in large calculations are plane waves and Gaussians. The latter do not constitute a complete and orthonormal set, and consequently quadruple sums over products of the basis functions are needed in evaluating some of the energy terms. This quickly becomes expensive. Using plane waves is equivalent to using an equally spaced grid in three space dimensions. If one needs a resolution good enough to describe core electrons in atoms, millions of plane waves are needed to represent the simplest unit cells. To overcome this problem, pseudopotentials can be constructed to eliminate the core orbitals. If these potentials are local, the computational task remains relatively manageable. However, to describe atoms such as oxygen nonlocal pseudopotentials are necessary. This leads to mixing of

the Fourier components of the basis with a considerable increase in the computational difficulty.

The finite element method¹¹ provides in principle an attractive alternative as a basis set. In this method, low-order polynomial *shape functions* are defined on a real space grid so that the functions are strictly zero outside their respective elements. The mesh can be varied so as to give high resolution where needed. If core orbitals are kept, this amounts to stretching the resolution near nuclei so that the important cusp condition can be fulfilled. It is also very easy to represent any function in terms of these shape functions. The method leads to a very sparse (but large) Hamiltonian and overlap matrices, which are nearly optimally amenable to iterative schemes such as the Car-Parrinello method. Moreover, fast algorithms (e.g. the multigrid technique¹²) are available for solving the Poisson equation using finite elements. Combining the methods listed above may eventually lead to breaking the bottleneck in very large electronic structure calculations with real atomic and molecular dynamics.

2.2. Effective-medium theories

Even with the increase in computing power and the ingenious new algorithms, the task of reliably calculating total energies for interacting atoms will long remain problematic in e.g. studying the dynamics of complex, low-symmetry extended defects. Another limitation of many first-principles calculations is that the amount of physical insight they directly provide is often

limited. In order to identify the important parameters and physical trends extendable to other systems simpler models have to be extracted and developed.

An alternative approach to calculating the total energy of a complicated system is provided by the effective-medium-theory¹³ in its various disguises. The simplest definition for these approaches is that they aim to go beyond the pair-potential description of condensed matter to include density-dependent interactions. The pair-potential model has serious drawbacks in applications to energetics of metallic and covalent solids (it may still be very useful for generating qualitative information such as the local configurations of atoms). For example, unless the elastic constants satisfy the Cauchy relation $C_{12} = C_{44}$, which is seldom true in real solids, an equilibrium pair potential cannot reproduce them. One suggestion to deal with this problem is to add to the total energy a term which depends on the macroscopic volume, by analogy with simple-metal pseudopotential perturbation theory. The volume-dependent term provides a fictitious external pressure, which balances the Cauchy pressure. It is however clear that the bulk modulus is no more uniquely defined (unless the volume-dependent term is linear in volume). This difficulty may lead to a gross misrepresentation of cohesive properties so that even qualitative simulating of such processes as crack opening or vacancy clustering, which involve volume changes, become suspect.

The basic idea behind the effective-medium theories is simple: the total energy of any given atom is determined by the effect of the surrounding atoms. In the spirit of density-functional theory, the electron density $n(r)$ is

singled out as the key variable. One writes a generically¹⁴

$$E_{\text{tot}}(N) = \sum_{i=1}^N F_i(n_i(\mathbf{R}_i)) + \frac{1}{2} \sum_{i,j} \Phi(\mathbf{R}_i - \mathbf{R}_j) + E^{\text{bs}}. \quad (1)$$

The first term is the "embedding" energy of an atom to its (instantaneous) environment; its dependence is through the electron density of all the other atoms. An ansatz for this is

$$n_i(\mathbf{R}) = \sum_{j \neq i} n_a(\mathbf{R}_i - \mathbf{R}_j), \quad (2)$$

where $n_a(\mathbf{R})$ is a density cloud associated with an atom at \mathbf{R} . The first term contains the leading many-atom contributions arising from the interaction of the atom with the electron density tails of all the other atoms. The function F can be calculated for a suitably chosen reference system. A particularly convenient one is the homogeneous electron gas, for which the embedding energies, screening clouds and associated electrostatic potentials can be calculated exactly. The second term is related to the electrostatic interaction between the embedded atoms, and the third term is the "band structure" energy related to the change in one-electron eigenvalues in going from the reference system to the real one. The third term is usually small in magnitude in metallic systems, but is important in determining e.g. the trends over transition metal series of the s-d hybridisation terms. The decomposition (1) bears resemblance to the familiar pseudopotential-based perturbation theory¹⁵ for simple metals, but is much

wider in applicability. There are several formulations based on (1) which differ in detail but conform to the same philosophy.

There is an ongoing effort to calculate the individual terms in the expansion (1) from first principles - with a minimum of adjustable parameters and uncontrolled approximations. In the formulation of Jacobsen *et al.*¹⁶, the function F is based on the homogeneous electron gas and reads

$$F(n) = \Delta E^{\text{hom}}(n) - \alpha n, \quad (3)$$

where

$$\alpha = - \int d\mathbf{r} \Delta \phi(\mathbf{r}). \quad (4)$$

Above, ΔE^{hom} is the embedding energy¹⁷ of an atom into a homogeneous electron gas of density n , and $\Delta \phi$ is the atom-induced change in the electrostatic potential of the jellium. Inserting (3) into Eq. (1) implies a self-consistency requirement in constructing the pseudoatom density clouds: $n_a(\mathbf{R})$ should be obtained from embedding the atom into a jellium characterised by the "tail summation" density $n_i(\mathbf{R})$. By going to the atomic-sphere-approximation, Jacobsen *et al.*¹⁶ discuss in detail the various cancellations and tail corrections in Eq. (1). As emphasized by these authors, the variational property of density-functional theory guarantees that independent approximations made in both the electron density and effective potential bring about only second-order

errors in total energy. This property is useful in seeking for convenient approximations in the evaluation of Eq. (1).

For perfect close-packed monoatomic solid the second term in Eq. (1) is nearly zero, and the cohesive energy per atom reduces to a very simple formula

$$E_{\text{coh}} = \Delta E^{\text{hom}}(n) - \alpha n + E^{\text{bs}} \quad (5)$$

$$= E_{\text{C}}(n) + E^{\text{bs}} \quad (6)$$

For simple metals even the band-structure term E^{bs} is small. Thus the position and depth in the minima of $E_{\text{C}}(n)$ (see Fig. 1.) determine the equilibrium lattice constant and cohesive energy. The bulk modulus is

$$B = (12 \pi S)^{-1} d^2 E_{\text{C}} / dS^2,$$

where S is the Wigner-Seitz radius. The equilibrium configuration is in general a result of the competition between inter-atomic electrostatic attraction ($-\alpha n$) and kinetic energy repulsion, which dominates $\Delta E^{\text{hom}}(n)$.

Jacobsen *et al*¹⁶ have also shown that Eq. (1), with appropriate account of the electrostatic second term, which is nonzero in a low-symmetry situation, can easily be used to analyze trends and even quantitatively predict energies associated with , say, surfaces and adsorbates. For example,

effective-medium theory offers a conceptually simple way of rationalizing the observations of surface relaxations on open fcc (110) surfaces of metals. The driving force behind the *inwards* relaxation of the first lattice plane is the attempt of these atoms to place themselves in the optimum electron density as defined by the minimum of the $E_c(n)$ curve of Fig. 1. The atoms in the first plane have fewer nearest neighbors than in bulk and subsequently sample too low a density, which is compensated for by moving closer to the second plane. The electrostatic term (beyond the atomic-sphere-approximation) opposes this trend and diminishes the relaxation. In fact this term, in combination with the increased density from the relaxed first layer, is responsible for the *outwards* relaxation of the second layer. For close-packed surfaces these two terms nearly cancel, but the more open the surface the stronger the driving force from the cohesive term $E_c(n)$. Similar considerations can be used to explain the stability of the missing-row reconstruction of some fcc (110) surfaces. Likewise, the tendency of adsorbed dimers on metals of (i) to have a shorter bond length than in vacuum and (ii) to rise slightly above the surface as compared to single adsorbates can be easily be qualitatively understood as arising from the same basic competition between the embedding cohesion and electrostatic repulsion.

Redfield and Zangwill¹⁸ have recently used the information contained in Fig. 1 to discuss the stability of icosahedral phases in Al-transition metal alloys. Fig. 1 shows that Al and Mn, for example, have very different optimum

density requirements. Redfield and Zangwill argue that the Mackay icosahedron encased in a shell of Al atoms is the optimum compromise for the structure of the alloy. It is also easy to see from Fig.1

that icosahedral binary alloys of Al are only formed with transition metals to the right of Ti in the Periodic Table.

2.3. Embedded-atom and related methods

The same basic physical considerations as discussed above are involved in the recent "embedded-atom"¹⁹ and "glue"²⁰ models for interatomic interactions. The total energy expression in these is very similar to that of Eq. (1):

$$E_{\text{tot}}(N) = \sum_{i=1}^N F_i(n_i(\mathbf{R}_i)) + \frac{1}{2} \sum_{i,j} \Phi(\mathbf{R}_i - \mathbf{R}_j). \quad (8)$$

However, in these approaches the functions F_i and Φ are empirically determined, obtained by choosing reasonable forms for the two functions and fitting to experiment. In particular, Daw *et al.*¹⁹ assumed the pair potential term Φ to be purely repulsive

$$\Phi_{AB}(R) = \frac{Z_A(R) Z_B(R)}{R}, \quad (9)$$

where Z_A and Z_B are (R -dependent) effective charges (> 0) of two embedded atoms A and B separated by distance R . The "many-body" potential function $F(n)$, dependent again on the electron density at the atom positions, starts from zero with a negative slope and positive curvature. It can be obtained by fitting²¹ the expression (3) to give the correct sublimation energy, lattice constant, elastic constants, vacancy formation energy etc., whereafter the model can be used in computer simulations of other more complicated phenomena²². The information used in the empirical fit actually only determines $F(n)$ and its first two derivatives for electron densities near the average host electron density n_{eq} . Foiles²² has argued that the zero pressure equations of state can be used to determine $F(n)$ for a larger class of electron densities. This is based on the ansatz of a "universal" equation of state suggested by Rose *et al.*²³ It should be noted, however, that the functions $F(n)$ in Eqs. (1) and (3) are not physically comparable; the latter is merely one possible parametrisation of the many-atom effects, while the first one actually obtains the function from embedding into the reference system.

Daw, Foiles and coworkers^{21,22} have applied their scheme to a large variety of important materials science problems. The computational cost does not significantly exceed that of pair potential simulations, once the functions F and ϕ are fitted. Ercolessi *et al.*²⁰ have used a very similar "glue" model to investigate the surface reconstruction of Au(100).

Finnis and Sinclair²⁴ have suggested yet another energy expression

which has resemblance to Eq. (1). In particular, they choose

$$F(n) = -A\sqrt{n}. \quad (10)$$

Moreover, n in their work is not interpreted as a density, but the rather the superposition is thought of in a more general sense that n_a in Eq. (2) is an adjustable function. The square root in Eq. (10) is chosen to mimic the result of tight-binding theory, in which n_a would be interpreted as a sum of squares of overlap integrals. This recipe and fit lead to an N-body potential applicable to bcc transition metals.

3. Computer simulations of structural properties

The above ideas have recently been applied in a number of computer simulation studies for materials problems of great practical interest. These include (i) sputtering and associated defect production²⁵ by hyperthermal ions near single-crystal surfaces, (ii) quenched-in structures²⁶ and collision cascades in amorphous solids, and effects associated with melting and solidification in constrained geometries and near surfaces and interfaces.²⁷ I choose to discuss one example of the latter the in some detail below.

3.1. Rare gas - metal interfaces

Noble gases are practically insoluble in metals and therefore show a strong tendency to precipitate into what are conventionally called bubbles even in the cases where the precipitate is in a solid phase. The pressure inside these bubbles can be enormous, up to several GPa. The precipitation tendency naturally arises from the strongly repulsive nature of the metal-rare gas interaction. In order to correctly characterize the gas densities and pressures inside these bubbles via a number of experimental probes²⁸ it has turned out to be important to have an accurate structural description of the interface between the metal and the gas.

We have undertaken a series of molecular dynamics simulations²⁹ for confined rare-gas bubbles. In general, large precipitates have three-dimensional faceted shapes. The problem of describing the atomic structure can therefore be approached by considering planar metal-noble gas interfaces representing the facets. A sandwich geometry was set up with six layers of metal atoms (up to 432 atoms) on each side of a collection of up to 600 gas atoms. Periodic boundary conditions were applied in all three directions. The interatomic potentials were specified according to effective-medium theory. In addition, a long-range van der Waals attraction adjusted to give correct physisorption properties of single gas atoms was added to the force law. The metal-metal potential reproduces well the bulk lattice constant, bulk modulus and

sublimation energy. The simulations were run up to 1500 hundred timesteps of 5×10^{-15} s after the system was first equilibrated to the required temperature.

Fig. 2 shows two examples of the perpendicular gas density profiles for He near an Al (100) interface. No solidification is observed in this case. With increasing mean density ρ_{He} defined as the average value for large z , a strong peak in the He density profile first develops near the Al surface and secondary peaks in the fluid follow. The surface peak originates from the statistical packing of atoms near the repulsive metal, much as with hard spheres near an impenetrable wall. The other peaks at higher fluid densities signal incipient ordering in the compressed fluid. The distance between the peaks corresponds to that between close-packed planes. No appreciable enhancement of the lateral ordering is observed in the He layer closest to the interface compared to the deeper layers.

Another set of simulations was performed for the Cu/Kr interface. In this case a solidification transition is observed. At high enough densities, there are *metastable* solid structures with lattice planes parallel to but incommensurate with the metal planes. These can be obtained from various starting arrangements with different packing densities. At lower gas densities, a fluid-like profile develops at the interface. The observed general features of the phase diagram are consistent with bulk Kr thermodynamical data.

Perhaps a more interesting observation concerns an "annealing" run, performed at Kr density of $2.5 \times 10^{22} \text{ cm}^{-3}$. The fluid was first equilibrated at a high temperature, whereafter temperature was lowered

below the solidification line. Time evolution of the system was then followed at a fixed temperature. In this case solid atomic planes nucleate from the interface (Fig. 3). The planes of Kr which start to condense parallel to the Cu surfaces are those of close-packed (111) character. They are not, however, perfect (111) planes, presumably due to the constraint of the periodic boundary conditions.

The observation that the close-packed (111) planes of the gas align themselves with the metal planes is also consistent with the experimental results of electron diffraction. It seems that the major criterion for the orientational relationship of the rare gas bubbles is that the close-packed planes of the gas are parallel to those of the host matrix (the latter presumably form the facets of the metal voids).

This result seems at first quite surprising, since the gas-metal interactions at the relevant distances are highly repulsive. One might have expected the gas to precipitate with a loosely packed plane next to a close-packed metal surface. In addition, since the gas-gas interactions are also repulsive at small distances, the close-packed gas has a higher surface energy than a more loosely-packed one. Finnis³⁰ has shown that the solution to the apparent paradox lies in the fact that a lowering of the bulk internal energy can be achieved with the epitaxial orientation, which more than outweighs the higher interfacial energy. Under high gas pressure and constant volume conditions the placing of low-index fcc (111) surfaces next to the metal facets is more than compensated by the relaxation of the bulk gas which this permits. While this result is seemingly independent of the actual orientation of the metal facets, the

edge effects inherent in the geometry used in the simulation might be important in establishing the rather small energy differences between hcp and fcc ordering.

Finally, there is an interesting connection between the molecular dynamics results and the experimentally observed superheating of rare gas precipitates in metals. Roussow and Donnelly³¹ reported a solid-fluid transition in Ar bubbles in Al 480 K above the bulk Ar melting temperature for the density question. The melting transition was deduced from the disappearance of electron diffraction spots associated with Ar. (The superheating effect is apparently much smaller or even absent for Kr in Cu and Ni.) Since the bubbles in general must be small to withstand the high pressures needed to solidify the fluid at high temperatures, a large fraction of the atoms will be at the bubble surface. Roussow and Donnelly³¹ discuss the surface effects in terms of reduced thermal vibrations of the gas atoms caused by the metal surface, which they present as a mechanism for suppression of the melting transition. The present molecular dynamics results suggest an alternative explanation, which may not be described as true superheating effect (it does not exclude that in the bubble interior melting takes place at the predicted bulk melting temperature). The peaks in the density profile even in the fluid phase are signature of ordering processes at the interface, which in a small bubble might yield a solid-like diffraction pattern above the bulk melting point of the solid. The inverse mechanism, surface-initiated melting or premelting has been observed in a number of computer simulations³² and, more recently, also in ion scattering experiments³³. The picture that is emerging from these studies is that melting

is initiated by a continuous lattice instability at the free surface and that the melting proceeds along directions of high packing density. This seems to be the case for a wide variety of interatomic potentials, including the angular three-body ones necessary to stabilise the tetrahedrally coordinated structures of Si and Ge³⁴.

4. Conclusions

To sustain the steady progress in expanding the scope and accuracy of electronic structure calculations, improvements are needed in algorithms used to solve the coupled problems of electronic (quantum) and ionic (classical) degrees of freedom. The recent ideas based on simulated annealing and related methods are most promising in this respect, and may well revolutionize and unify the traditionally somewhat separate fields of electronic structure calculations and classical molecular dynamics simulations. Also the questions of completeness and manageability of basis sets in large calculations are subject to new scrutiny. On the other hand, the development of simple but transparent schemes such as the effective-medium theory and related approaches is most helpful from both pragmatic and conceptual points of view.

Eventually the limiting obstacle in detailed understanding of chemical and structural problems lies in the level of description of electronic exchange and correlation effects. While the local-density approximation of

density-functional theory has proven surprisingly robust and reliable, its validity is fundamentally limited³⁵. Efforts to improve and generalize it are thus very worthwhile.

Acknowledgments

This work was supported in part by grants from the Petroleum Research Fund, administered by the ACS, and the Office of Naval Research, Grant No. N00014-82-K-0576.

References

1. See e.g. Computer-Based Microscopic Description of the Structure and Properties of Materials, eds. J. Broughton, W. Krakow and S.T. Pantelides (Materials Research Society 1986)
2. B.J. Alder and T.E. Wainwright, J. Chem. Phys. **27**, 1208 (1957)
3. See e.g. M. Manninen, P. Jena, R.M. Nieminen and J.K. Lee, Phys. Rev. **B18**, 7057 (1981) and references therein
4. F.H. Stillinger and T.A. Weber, Phys.Rev. **B31**, 5262 (1985); R. Biswas and D.R. Hamann, Phys.Rev. Lett. **55**, 2001 (1985); J. Tersoff, Phys.Rev.Lett. **56**, 632 (1986)
5. S. Kirkpatrick, C.D. Gelatt and M.P. Vecchi, Science **220**, 671 (1983)
6. R. Car and M. Parrinello, Phys.Rev.Lett. **55**, 2471 (1985)
7. M.C. Payne, P.D. Bristowe and J.D. Joannopoulos, Phys.Rev.Lett. **58**, 1348 (1987)
8. D. Hohl, to be published
9. J.M. Soler and A.R. Williams, to be published
10. J. Pehr and R.M. Nieminen, to be published
11. See e.g. G. Dhatt and G. Touzot, The Finite-Element Method Displayed (Wiley, New York 1982)
12. Multigrid Methods, eds. W. Hackbusch and U. Trottenberg (Springer, Heidelberg 1982)
13. J.K. Nørskov and N.D. Lang, Phys.Rev. **B21**, 2131 (1980); M.J. Stott and E. Zaremba, Phys.Rev. **B22**, 1564 (1980); J.K. Nørskov, Phys.Rev. **B26**, 2875 (1982)
14. M. Manninen, Phys.Rev. **B34**, 8486 (1986)

15. W.A. Harrison, Pseudopotentials in the Theory of Metals (Benjamin, New York 1966)
16. K.W. Jacobsen, J.K. Nørskov and M.J. Puska, to be published
17. M.J. Puska, R.M. Nieminen and M. Manninen, Phys.Rev. **B24**, 3037 (1981)
18. A.C. Redfield and A. Zangwill, to be published
19. M.S. Daw and M.I. Baskes, Phys.Rev.Lett. **50**, 1285 (1983); Phys.Rev. **B29**, 6443 (1984)
20. F. Ercolessi, E. Tosatti and M. Parrinello, Phys.Rev.Lett. **57**, 719 (1986); Surf.Sci. **177**, 314 (1986)
21. S.M. Foiles, M.I. Baskes and M.S. Daw, Phys.Rev. **B33**, 7893 (1986)
22. S.M. Foiles, Phys.Rev. **B32**, 3409 (1985); Phys.Rev. **B32**, 7685 (1985)
23. J.H. Rose, J.R. Smith, F. Guinea and J. Ferrante, Phys.Rev. **B29**, 2963 (1984)
24. M.W. Finnis and J.E. Sinclair, Phil.Mag. **A50**, 45 (1984)
25. S. Valkealahti and R.M. Nieminen, Nucl.Inst.Meth. **B18**, 365 (1987); for a review, see H.H. Andersen, Nucl.Inst.Meth. **B18**, 321 (1987)
26. J. Laakkonen and R.M. Nieminen, J. Non-Cryst.Sol. **75**, 237 (1985) and to be published.
27. See e.g. Structure and Dynamics of Surfaces I, eds. W. Schommers and P. von Blanckenhagen (Springer, Heidelberg 1986)
28. S.E. Donnelly, Radiat.Eff. **90**, 1 (1985)
29. K.O. Jensen and R.M. Nieminen, Phys.Rev. **B35**, 2087 (1987) and to be published
30. M. W. Finnis, to be published
31. C.J. Roussow and S.E. Donnelly, Phys.Rev. Lett. **55**, 2960 (1985)
32. See e.g. J. Broughton and G.H. Gilmer, J. Chem. Phys. **79**, 5105 (1983); Phys.Rev. Lett. **56**, 2692 (1986)
33. J.W.M. Frenken and J.T. van der Veen, Phys.Rev.Lett. **54**, 134 (1985)
34. J. Lampinen and R.M. Nieminen, to be published
35. W. Pickett, Comments on Solid State Phys. **12**, 1 (1985)

Figure Captions

Fig.1. The energy $E_C(n)$ (see Eq. (6)) as a function of electron density n for various elements. After refs. 16 and 17.

Fig.2. The simulated perpendicular density profiles for pressurized He fluid near Al(110) wall. $T = 300$ K. After ref. 29.

Fig. 3. The simulated nucleation as a function of time (b - c) of solid Kr(111) layers near a Cu(100) interface after quenching from the melt (a). After ref. 29.

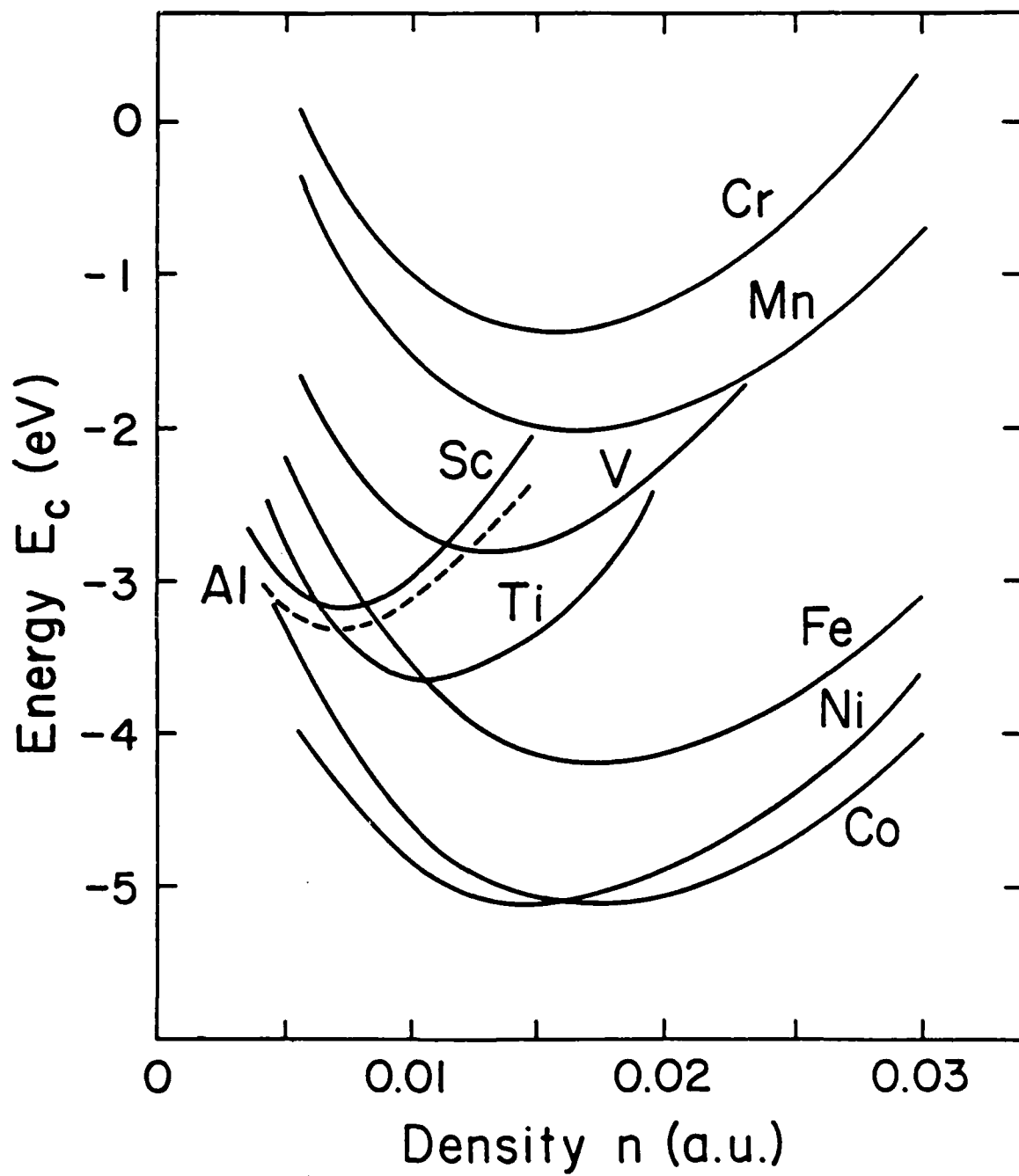


Fig. 1.

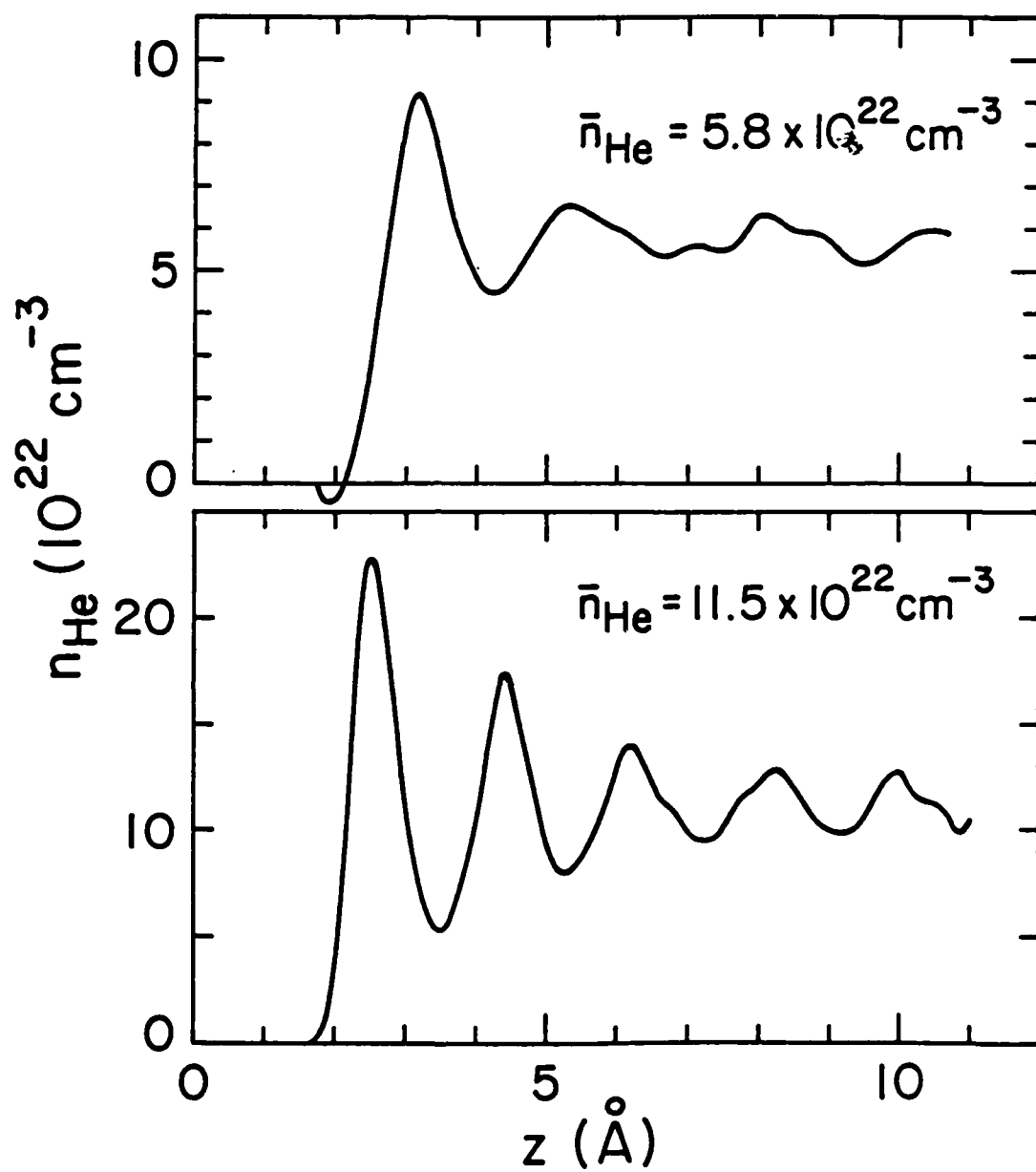


Fig. 2

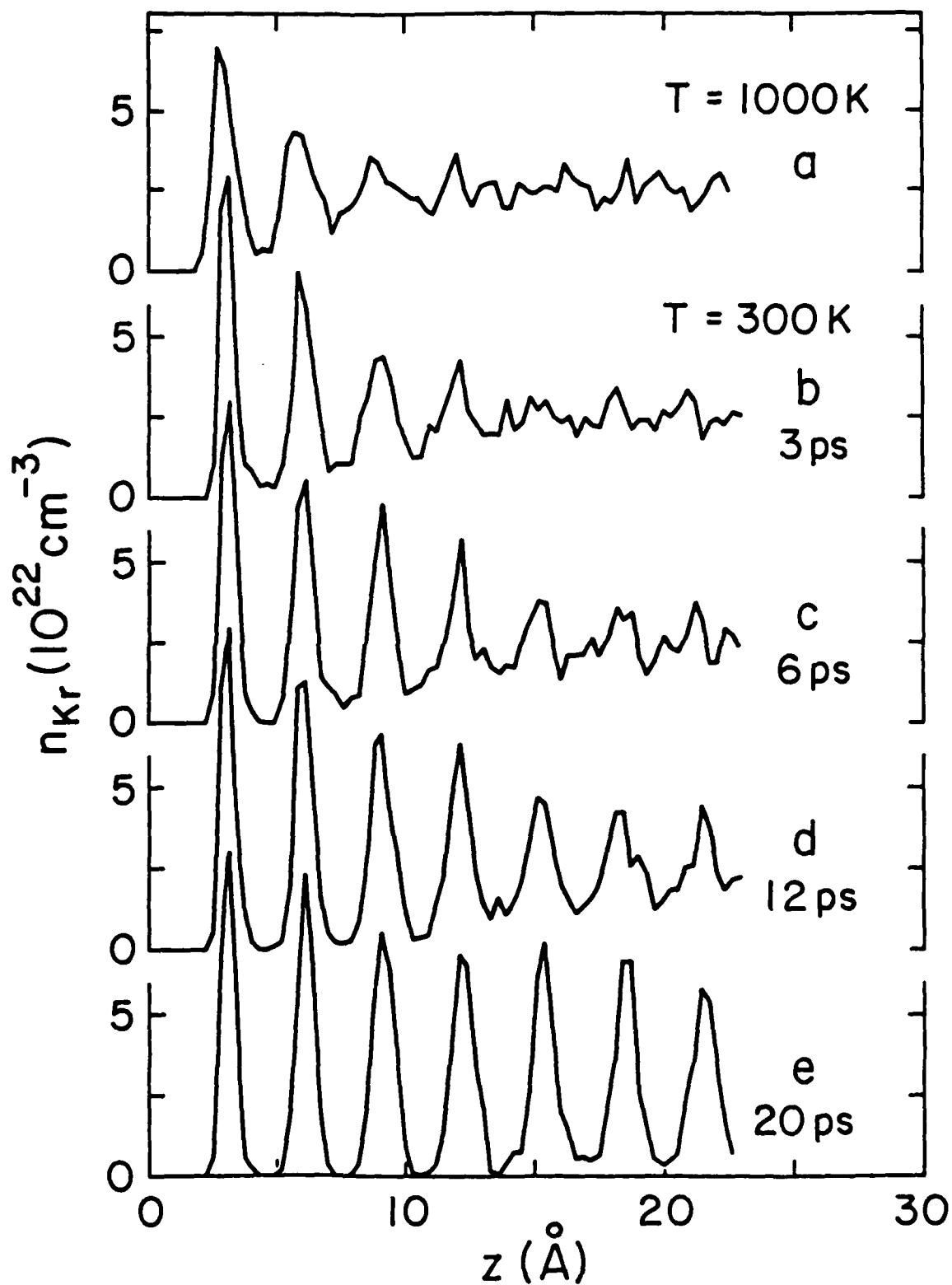


Fig. 3

END

10-87

DTIC